

Thermodynamical Signatures of an Excitonic Insulator

Benno Bucher

HSR Hochschule für Technik, 8640 Rapperswil, Switzerland

Tuson Park, J. D. Thompson

Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Peter Wachter

Lab. für Festkörperphysik, ETH Zürich, 8093 Zürich, Switzerland

(Dated: February 23, 2008)

In the 1960s speculations arose if a ground state exists in solid state materials with an electron and a hole bound to a pair with their spins added to integer values, i.e. excitons. Here we show that electrons and holes in $\text{TmSe}_{0.45}\text{Te}_{0.55}$ do form excitons as the thermodynamical ground state. The formation of a large number of excitons in an indirect gap semiconductor requires momentum conservation by means of phonons and, hence, implies a significant change of the heat capacity of the lattice, as found experimentally. The thermodynamically derived phase diagram sustains a bosonic ground state in condensed matter.

The band structure of metals, semiconductors and insulators is the consequence of the fermionic character of the electrons. However, if an electron is excited out from the valence band, a positively charged hole stays behind, attracting the negatively charged electron due to the Coulomb attraction. A bound electron-hole pair is called an exciton; such a quasiparticle is a boson since the individual spins add to spin zero or one (see Fig. 1). Mott [1] suggested that a semimetal (SM) is unstable against the formation of such a bound electron-hole pair because the small density of free electrons does not screen the Coulomb attraction. Knox [2] realized that the band structure of a semiconductor (SC) might also be unstable against the spontaneous formation of excitons if the binding energy of the exciton is larger than or comparable to the energy gap. The notion of the excitonic insulator (EI) has been coined.

The elaboration of the theoretical concept of excitonic insulators provided insights into the possible mechanism of how a new ground state could form [3]. Weakly bound excitons should reveal a simultaneous formation and phase coherence, as within BCS theory; whereas, strongly coupled excitons form at high temperatures and are subject to a Bose condensation (BC) at a lower temperature. The crossover from weak to strong coupling became essential for understanding the high temperature superconductors. The Bose statistics of the excitons would initiate new features and promise new effects and applications [4]

The experimental realization of a bosonic ground state has concentrated on excitons in semiconductors. However, in this class of materials the excitons are not in the energetically lowest state but laser excited particles. A steady state equilibrium between optical generation of the excitons and the decay within their life time must be achieved [5]. Our approach has been the application of pressure in order to lower and fine-tune the energy of the

excitons to the energy level of electrons in the valence band (see Figure 1).

$\text{TmSe}_{0.45}\text{Te}_{0.55}$ is a narrow gap semiconductor. Chemistry would suggest the valences $\text{Tm}^{+2}[\text{Se}_{0.45}\text{Te}_{0.55}]^{-2}$ for the ionic binding regime but, actually, the small energetic separation of the 4f states from the conduction band causes a 4f-5d hybridization with the result of a so-called intermediate valent state $\text{Tm}^{+2.2}$ where the generally localized 4f states acquire a narrow (some tens of meV) wide 4f valence band. At 300 K the energy gap closes on applying pressure [6] and there is a transition from a semiconductor to a ferromagnetic semimetal. But at temperatures below 250 K, the resistivity increases strongly in the pressure range between 5 and 8 kbar, despite of the anticipated closing of the gap. Hall effect measurements [7] reveal that the anomaly is due to localization of electrons (inset to Fig. 2 a) as demanded by a formation of excitons with their energy level crossing the high density of states of the quasi-localized 4f electrons around 5 kbar (Fig. 1).

Further hints to a new phase have come from heat transport. Thermal conductivity [8] showed a first order jump, like the resistivity, giving heat conductivity below 20 K that is higher than in the semimetal state. A phase diagram has been deduced out of these data of the transport properties (Fig. 2a). Yet the formation of a new phase must be corroborated by thermodynamics. This was the motivation to measure the heat capacity and to establish the existence of a new thermodynamical phase.

A self-clamping CuBe pressure cell has been used with a silicon-based pressure transmitting fluid. A superconducting lead manometer was employed as the pressure gauge. The pressure was not constant on cooling down but rather follows a pressure path that depends on the cell and the starting pressure. [9]. An ac calorimetry technique [10] was adapted for studying phase transitions at hydrostatic pressure. With this technique, a small si-

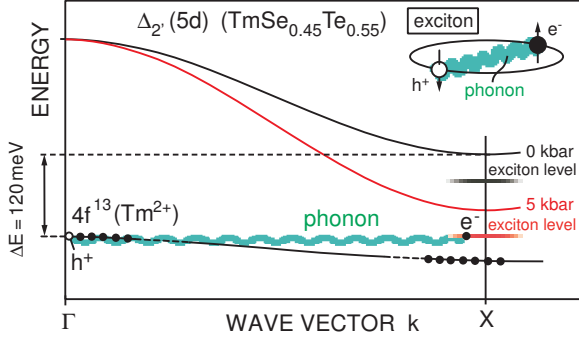


FIG. 1: Schematic illustration of the band structure of $\text{TmSe}_{0.45}\text{Te}_{0.55}$ on applying external pressure. Exciton levels below the X point of the Brillouin zone reduce their separation to the quasi-localized $4f^{13}$ electrons of Tm^{2+} . Around 5 kbar, it becomes energetically favorable for an electron to occupy the excitonic energy level, leaving behind a positively charged hole. Conservation of momentum requires the binding of a phonon with a wave vector from the Γ to the X point.

nusoidal heat input is supplied to the sample ($1 \times 1 \times 0.2 \text{ mm}^3$) through a constantan wire bent to a meander-like structure attached to one side of the sample. The resulting temperature oscillation was detected by a Chromel-Au/Fe thermoelement attached to the other side of the single crystal. At steady state, the time-average temperature T_1 of the sample is larger than the bath temperature (pressure medium). In addition, there is a small temperature oscillation about T_1 with a peak-to-peak temperature ΔT_{ac} . Under optimal conditions of the ac frequency, ΔT_{ac} is directly related to the heat capacity. However the calculation of the absolute value of the heat capacity would require the knowledge of thermal resistances to the bath and the thermometer. In the absence of this information, the absolute value of heat capacity was estimated by scaling the high-temperature ac heat capacity to the Dulong-Petit value of $\text{TmSe}_{0.45}\text{Te}_{0.55}$ of $52 \text{ J/mol K per f.u.}$ However, some influence of the pressure transmitting fluid can not be prevented; thus, conclusions are based mainly on differential changes of the heat capacity. With this technique, phase transitions also manifest themselves through a marked phase shift of the thermo-signal across the sample.

Figure 2 b) shows the ac heat capacity C_{ac} for selected pressure runs. The pressure inside the self-clamped cell reduces on cooling, as determined in independent measurements, and, consequently, the heat capacity could be measured neither at constant pressure nor at constant volume. Depicted are the ac heat capacities of representative pressure runs K, L, M, N and zero pressure (black). The heat capacities show a conventional curvature for a Debye-like phonon density of state at zero pressure and in the metallic regime. The phase boundary from semiconducting to phase A is reflected as a large

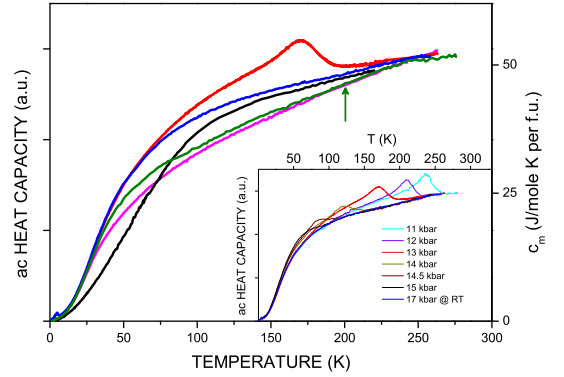
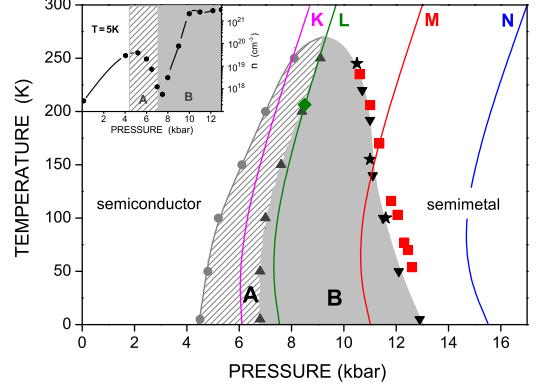


FIG. 2: Heat capacity of $\text{TmSe}_{0.45}\text{Te}_{0.55}$ at high pressures a) Phase diagram constructed from a number of different measurements: \bullet (gray) onset of resistivity increase; \blacktriangle maximum of resistivity; \blacksquare maximum of ac heat capacity; \star first order transition of heat conductivity; \blacktriangledown first order transition of resistivity and \blacklozenge the onset of deviation of ac heat capacity of pressure run L. The inset shows the pressure-dependent Hall number n at 5 K [7], where n decreases in phase A and electrons start to delocalize again in phase B. b) ac heat capacity data for different pressure runs: black (zero pressure), red (run M), blue (run N, metallic), green (run L) and magenta (run K). A ferromagnetic phase transition at 6 K is discernible in the metallic phase. The inset to Fig. 2 b) represents the experimental results for seven pressure runs that cross the semimetal to phase B boundary. Peaks in C_{ac} (\blacksquare) are denoted in Fig. 2 a). The green arrow indicates the phase transition from phase A to phase B.

change in slope of the heat capacity of run K around 250 K, signalling a second order phase transition. The reduced heat capacity of run K below 250 K (20 meV) indicates thermally no longer activated lattice vibrations. The quasi-localization of free carriers starts below the same temperature [6]. Indeed, wave-vector conservation upon the formation of excitons in an indirect gap semiconductor implies the binding of high energy phonons at the boundary of the Brillouin zone to form excitons (Fig.

1). The number of excitons is then given approximately by the decrease in free-carrier density, measured by the Hall number [7]: $\Delta n_{max} \simeq 10^{20} \text{ e}^-/\text{cm}^3$. The heat capacity of run K is nearly linear between 100 to 250 K, which points to a constant phonon density of states. The reduced heat capacity also implies a stiffer lattice [11], [8].

Pressure run L enters phase B from phase A around 200 K. Only 1 kbar higher in the semimetal phase, the heat capacity changes its shape qualitatively (inset to Fig. 2b). Pressure run M enters phase B from the semimetal side and a giant change takes place below 200 K. In the metallic region (run N) the heat capacity recovers a conventional Debye-like curvature but with a lower Debye temperature Θ_D , as expected for intermediate valent systems at higher pressures [8].

By subtracting the heat capacity of run N, the specific heat of the runs from the metallic region into phase B can be decomposed into a phononic part and a contribution ΔC belonging to the phase transition. A fit of the extra heat capacity ΔC reveals a Gaussian peak together with a broader contribution at lower temperatures (Fig. 3). A Gaussian shape of the heat capacity is known for first order transitions [12] as a temperature gradient is always present [13]. Furthermore, neutron measurements [6] show an isostructural phase transition with an expansion of the volume by 4.8% at the phase boundary from semimetal to phase B (inset to Fig.3). This expansion of the lattice increases the pressure inside the self-clamped pressure cell, counterbalancing the phase transition. A first order transition also has been observed in the resistivity [6], Hall constant [7] and heat conductivity [8].

The broadening of the transition allows calculation of the entropy change and, therefore, a verification of the Clausius- Clapeyron relation:

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta Q}{T \cdot \Delta V} \quad (1)$$

The slope $\frac{dp}{dT}$ on the left side of Eq. (1) can be determined from the phase boundary shown in Fig. 2a and gives $-5.2 \cdot 10^5 \text{ J/m}^3 \text{ K}$ at 200 K. For the right side of Eq. (1), the corresponding change of entropy at the boundary (dark gray shaded peak in Fig. 3) provides $\Delta S=0.8 \text{ J/mol K}$. With a volume expansion of $1.56 \cdot 10^{-6} \text{ m}^3/\text{mol}$, the resulting $\Delta S/\Delta V = -5.1 \cdot 10^5 \text{ J/m}^3 \text{ K}$ is in excellent agreement with the slope of the phase boundary. The additional broad heat capacity at lower temperatures comprises $\Delta S=1.6 \text{ J/mol K}$ and, hence, gives a total change of entropy of 2.4 J/mol K (inset to Fig. 4).

Figure 4 shows the additional contribution $\Delta C/T$ for the pressure runs into phase B. The change of entropy due to entering phase B from phase A was estimated by subtracting the heat capacity of run K from run L (green curve in Figure 4). The total change of entropy is similar for all runs.

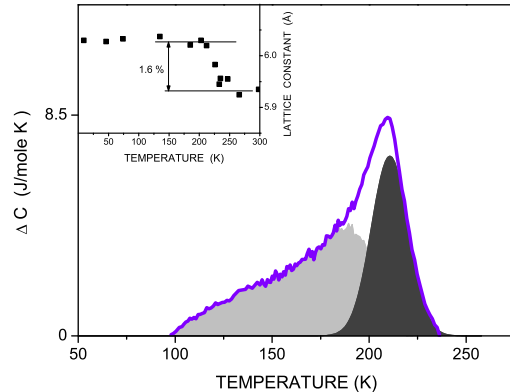


FIG. 3: Heat capacity for the violet pressure run (11.8 kbar at 5 K, Fig. 2b) after subtracting the conventional background characterized in run N. A fit of the extra heat capacity ΔC reveals a Gaussian peak (dark gray) together with a broader contribution at lower temperatures (light gray). The dark gray area reflects a latent heat. The accompanying expansion of the lattice increases the pressure inside the self-clamped pressure cell counterbalancing the phase transition. The inset shows the large lattice expansion at the same pressure [6].

Let us first discuss the first order phase transition into phase B. The spin entropies for the thulium ions are $S_{spin}/k_B = \ln(2J+1) = 2.08$ for Tm^{+2} ($J = \frac{7}{2}$) and 2.56 for Tm^{+3} ($J = 6$), respectively. A gain of entropy by a valence change from Tm^{+3} to Tm^{+2} would result in $\Delta S_{spin} = 0.48 \cdot k_B = 3.98 \text{ J/mol K}$, in good agreement with the experimental result shown in the inset of Fig. 4. The first order expansion of the lattice might then solely be a consequence of the larger Tm^{+2} ions. The f-electron intra-site Coulomb repulsion does not favor this picture and, particularly, the Hall measurements show that electrons in phase B are not localized as they are in phase A [7]. The electrons in phase B seem to compensate the local magnetic moment of the Tm ions but are not localized on the Tm site itself. The idea of electrons redistributed over d-orbitals that are bound to its original anion site, i.e. excitons, also has been used to explain the golden phase of SmS [14],[15].

The expansion of the crystal at the first order phase transition against the pressure medium ($\approx 12 \text{ kbar}$) requires an energy $\Delta E_{elastic} = p \cdot \Delta V \approx 1800 \text{ J/mol} = 20 \text{ meV/f.u.}$ This value is to be compared with the latent heat $L = \Delta S \cdot T = 165 \text{ J/mol} = 1.7 \text{ meV/f.u.}$ The spin entropy which usually drives the Kondo and Kondo - lattice effects in highly correlated electron systems can not explain the phase transition. Only an electronic energy could account for the large energy per formula unit; the binding energy of excitons is in this range. This formation of excitons has been predicted for electrons in $\text{TmSe}_{0.45}\text{Te}_{0.55}$ interacting via a statically screened

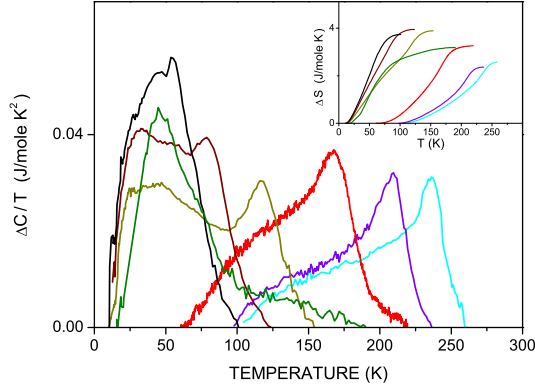


FIG. 4: $\Delta C/T$ for different pressure runs. The pressures at low temperatures are from right to left: cyan (10.7 kbar), violet (11.8 kbar), red (11.9 kbar), dark yellow (13.5 kbar), brown (13.7 kbar), black (13.9 kbar) and green (7.6 kbar). The change of entropy due to entering phase B from phase A was calculated by subtracting the heat capacity of run K from run L (green curve). The inset shows the integrated area of $\Delta C/T$, which corresponds to the involved change of entropy and is about the same for all pressure runs.

Coulomb potential [16]. The broad contribution to the heat capacity in phase B (Fig. 3) could be attributed to the continuous formation of bound excitons. But the formation of a large number of excitons with heavy holes is subject to crystallization [3] and the first order transition could indicate a melting process.

The localization of the electrons in phase A [7] is accompanied by the disappearance of phonons (below 250 K of run K in Fig. 2b) as expected at the formation of a large number of excitons in an indirect gap semiconductor. Hence, the insulating phase A could be interpreted by the opening of a "many-body gap", i.e. the proposed Bose condensate of excitons [17]. The ground state of an excitonic insulator in an indirect gap semiconductor competes with an instability to an electron - hole liquid [3]. But the asymmetry of electron to hole mass of $m_h/m_e \approx 80$ may prevent the e-h liquid instability in $\text{TmSe}_{0.45}\text{Te}_{0.55}$ and favors crystallization in a two-component Coulomb system [18]. Even more significant might be the fact that the movement of holes is inherently related to a change of the local magnetic moment. A magnetic binding energy may then support the formation of hole - electron bosons.

In summary ac heat capacity measurements of

$\text{TmSe}_{0.45}\text{Te}_{0.55}$ at high pressure have revealed a pronounced change in the phonon spectrum up to 250 K. The binding of a large number of high energy phonons is in agreement with the formation of an excitonic insulator phase. The gain of spin entropy points to the formation of singlet excitons.

The authors thank F. Bronold, H.Fehske, and A. Schilling for valuable discussions. Work at Los Alamos was performed under the auspices of the US DOE, Office of Science. Correspondence and requests for further information. should be addressed to Benno Bucher (email: bbucher@hsr.ch).

-
- [1] N. Mott, *Philos. Mag.* **6**, 287 (1961).
 - [2] R.S. Knox, *Solid State Physics*, Eds. F. Seitz, D. Turnbull and H. Ehrenreich (Academic Press Inc, New York, 1963) Suppl. 5, p 100.
 - [3] For example see: B. Halperin and T. Rice, *Solid State Physics*, Eds. F. Seitz, D. Turnbull and H. Ehrenreich (Academic Press Inc, New York, 1968) Vol. 21.
 - [4] M. Rontani and L. J. Sham, *Phys. Rev. Lett.* **94**, 186404 (2005).
 - [5] For a review see: P.B. Littlewood *et. al.*, *J. Phys.: Condens. Matter* **16**, S3597 (2004).
 - [6] J. Neuenschwander and P. Wachter, *Phys. Rev. B* **41**, 12693 (1990).
 - [7] B. Bucher, P. Steiner, and P. Wachter, *Phys. Rev. Lett.* **67**, 2717 (1991).
 - [8] P. Wachter, B. Bucher, and J. Malar, *Phys. Rev. B* **69**, 094502 (2004).
 - [9] J.D. Thompson, *Rev. Sci. Instr.* **55**, 231 (1984).
 - [10] P. Sullivan and G. Seidel, *Phys. Rev.* **173**, 679 (1968).
 - [11] For example see: T.H.K. Barron and G.K. White, *Heat Capacity and Thermal Expansion at Low Temperatures* (Kluwer Academic, New York, 1999)
 - [12] A. Schilling *et.al.*, *Phys. Rev. Lett.* **78**, 4833 (1997).
 - [13] This phenomenon is similar to boiling a pot of water: the water does not instantly turn into gas, but forms a turbulent mixture of water and water vapor bubbles. Furthermore if a substance as water and $\text{TmSe}_{0.45}\text{Te}_{0.55}$ expands upon cooling the effect called regelation takes place: melting under pressure and freezing again when the pressure is reduced.
 - [14] K. Matsubayashi *et.al.*, *J. Jap. Phys. Soc.* **76**, 033602 (2007).
 - [15] K.A. Kikoin, *Sov. Phys. JETP* **58**, 582 (1983).
 - [16] F.X. Bronold and H. Fehske, *Phys. Rev. B* **74**, 165107 (2006).
 - [17] Ji-Min Duan, D.P. Arovas, and L. J. Sham, *Phys. Rev. Lett.* **79**, 2097 (1997).
 - [18] M. Bonitz, V.S. Filinov, V.E. Fortov, P.R. Levashov, and H. Fehske, *Phys. Rev. Lett.* **95**, 235006 (2005).